STUDIES ON SOME BIOINSPIRED MATERIALS IN SOLAR ENERGY INDUCED WATER SPLITTING FOR HYDROGEN GENERATION

A Synopsis Submitted For Partial Fulfilment Of The Requirement For The Degree Of Doctor Of Philosophy In Chemistry

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1. INTRODUCTION

1.1 NEED OF ALTERNATIVE CLEAN FUEL: *For sustainable development*

Our dependency on instant energy has expanded at an unprecedented pace because of which the future energy demand is expected to increase significantly. The global energy consumption rate is set to grow by 2.3% yr^{-1} from 16.3TW (in year 2012) [1] to 20 TW by year 2030, doubled by 2050 and tripled by the end of century [2]. About 85% of the total global energy consumed at present comes from burning fossil fuel with the proportion approaching 90% for developed countries [3]. However, fossil fuels are unevenly spread over the planet and they are depleting at a faster pace. In addition to this, production, transmission and use of fossil fuels are posing serious threat to the environment. The combustion of fossil fuel generates CO_2 which play vital role in global climate change. The replacement of fossil fuels by a clean, renewable and sustainable energy source is a major challenge for the scientists and technologists of present generation.

Efficient use of solar energy could help in overcoming many energy and environmental issues, as the solar energy received by the Earth surface is 1.3×10^5 TW and it exceeds almost four times the current global human energy consumption [3]. It is interesting to note that the total amount of energy accumulated in all fossil resources corresponds to the solar energy received by the earth over a short duration of 7 days [4]. However, sunlight is intermittent source of energy and the supply is not synchronised with continuous demand, therefore the direct use of solar energy is limited at present [5].

Among various alternatives, hydrogen as fuel offers highest potential benefits in terms of reduced emissions of greenhouse gases, various pollutants and diversified supply. Environmentalists have promoted hydrogen fuel as solution for existing problem of global warming and climate change. The important criteria for an ideal fuel are cleanliness, inexhaustibility and convenience. Hydrogen possesses all these properties and emerges as an environment friendly substitute for fossil fuels [6-10].

1.2 HYDROGEN: *For Fuelling The Future*

Hydrogen is the smallest and the simplest molecule, having an important role in the global energy economy [11]. It is widely considered as a promising energy carrier. Hydrogen is a clean material, because the combustion of H_2 produces only pure water with a large amount of heat release.

$$\mathbf{H_2 + 1/2O_2 \longrightarrow H_2O;\ \Delta G^\circ = -237\ kJ\ mol^{-1}}\ [4]$$

In ambient conditions, hydrogen is non reactive while on the other hand, hydrogen atom is chemically very reactive and it is not found in free state in nature. Very high temperature is required to dissociate molecular hydrogen into its atomic form [12].

Some desirable properties of hydrogen are:

- *hydrogen is a very light gas* ***~ 0.08988 gL^{-1}****, the energy density of hydrogen is much higher than any other fuel such as gasoline.*
- *for one gram of hydrogen,* ***~140 kJ*** *of energy can be released, which is almost four times higher than methane ~* ***33 kJg^{-1}***
- *energy storage capacity per mole is* ***119kJg^{-1}*** *while that of oil is* ***40 kJg^{-1}***
- *it is non toxic*
- *combustion produces steam and liquid water*
- *it is easily assimilated in the biosphere and recycled by plant*
- *used as feedstock for the chemical industry for the production of chemicals and petrochemicals*

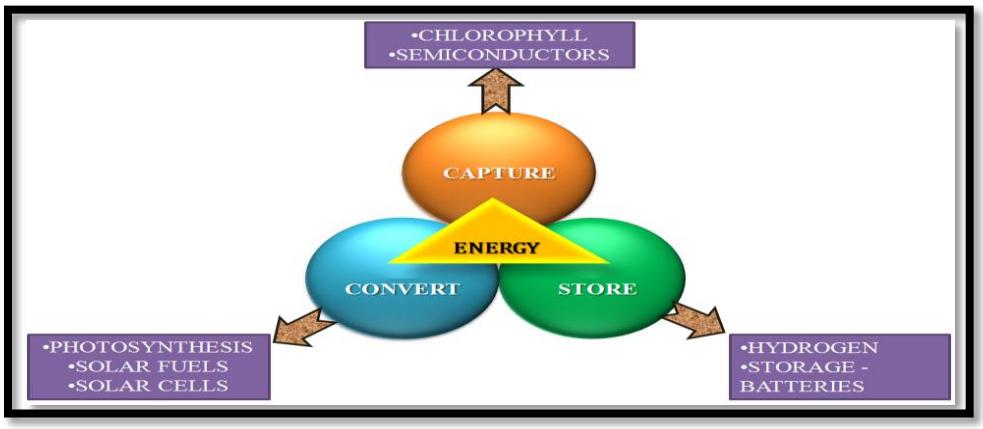


Fig. 1.1 Integration of systems that capture photons, convert light energy into electricity or fuels, and stored energy is crucial for harvesting solar energy.

Hydrogen can be produced via number of different ways as given below:

- Thermochemical Method – based on thermal and chemical energy for water electrolysis
- Biochemical Method – uses biological species (such as bacteria, fungi) which are involved in splitting of water based on fermentation process
- Electrolytic Method – uses external bias to split water
- Photoelectrochemical and Photocatalytic Method – uses photon energy for electrolytic dissociation of water into hydrogen and oxygen gas

Out of the various methods of hydrogen production, photoelectrochemical (PEC) is considered superior because of inherent advantages, such as:

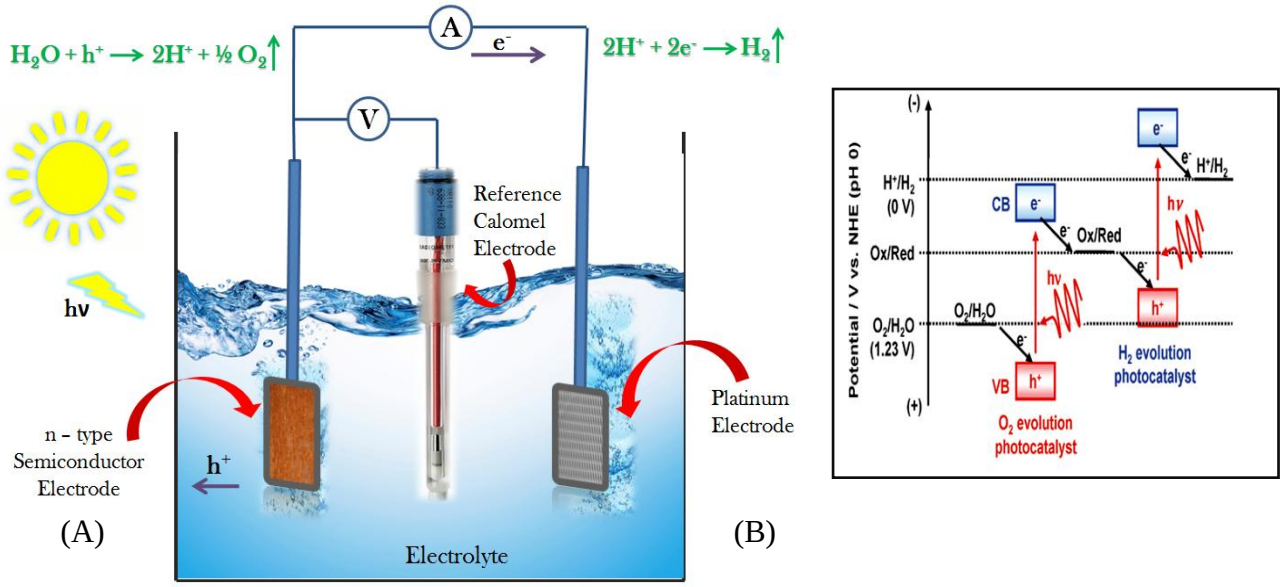
- *PEC technology is based on solar energy and water both of which are abundant in nature.*
- *PEC technology is environmentally safe.*

- *PEC technology results in no undesirable by-products.*
- *PEC technology can be used on both small and large scales industries.*

1.3 PHOTOELECTROCHEMICAL WATER SPLITTING: *Artificial Photosynthesis*

PEC route is a single step, direct conversion process for hydrogen production. It is environmental friendly method using renewable resources such as water and solar energy. The first demonstration of PEC water splitting was given by Honda and Fujishima in year 1972 using TiO_2 (n-type) semiconductor photoanode.

PEC set up consist of light sensitive semiconductor as working electrode, platinum as counter electrode and calomel as reference electrode, all immersed in aqueous electrolyte [16]. With exposure to sunlight, photon induced electron-hole pairs are formed in the semiconductor; which then interact with ionic species of electrolyte at solid/liquid interface. Photoexcited holes drive the oxygen evolution reaction (OER) at the anode surface while photoexcited electron are responsible for carrying out the hydrogen evolution reaction (HER) at the cathode surface in n-type semiconductor electrode [13;14].



1.2 (A) Schematic diagram of photoelectrochemical cell consisting of n-type semiconductor photoanode, reference (SCE) and metal cathode for water splitting [15]. (B) Two step excitation – Z scheme [3]

HEART OF PEC SYSTEM: *Semiconductor Electrodes*

The main component of the PEC cell is the semiconductor electrode. Every semiconductor is characterised by a unique bandgap. The maximal photon to current conversion efficiency of

photoelectrochemical devices can be achieved at band gap 1.8 – 2.2eV including over potential losses.

Water photo-electrolysis using a PEC involves several processes within the photo-electrodes and at the photo-electrode/electrolyte interface, including [16]:

- *light-induced intrinsic ionization of the semiconducting material (the photoanode), resulting in the formation of electronic charge carriers (electrons and holes);*
- *oxidation of water at the photoanode by holes;*
- *transport of H^+ ions from the photoanode to the cathode through the electrolyte and transport of electrons from photoanode to the cathode through the external circuit;*
- *reduction of hydrogen ions at the cathode by electrons.*

For an ***alkaline electrolyte***, the reduction and oxidation reactions can be written as [17]:

$$4H_2O + 4e^- \rightleftharpoons 2H_2 + 4OH^- \qquad E^0_{red} = -0.828V \text{ vs. NHE}$$
$$4OH + 4h^+ \rightleftharpoons 2H_2O + O_2 \qquad E^0_{ox} = -0.401V \text{ vs. NHE}$$

For an ***acidic electrolyte***, the reduction and oxidation reactions can be written as:

$$4H^+ + 4e^- \rightleftharpoons 2H_2 \qquad E^0_{red} = +0.000V \text{ vs. NHE}$$
$$2H_2O + 4h^+ \rightleftharpoons 4H^+ \qquad E^0_{ox} = -1.229V \text{ vs. NHE}$$

Major setback associated with the present system:

- *Even after four decades of extensive research, a visible light driven, efficient and stable water splitting system still remains an elusive goal.*
- *Efficiency and stability is a major concern to achieve the desired efficiency target of 10% which is a prerequisite for commercialization [18].*
- *At present, stable metal oxide based PEC semiconductor materials have low efficiency while high efficiency semiconductors are unstable and degrade within a short time [19;20;21;22].*
- *Large band gap of working electrode and fast charge recombination also create hurdles in the existing system*

1.4 NATURE'S EFFICIENT LIGHT HARVESTING METHOD: *Photosynthesis*

Both PEC system and naturally occurring photosynthesis process use solar energy, however they operate in different ways. Photosynthesis is a natural nanotechnology system using

macromolecular machines (photosystems) that catalyze solar energy driven water splitting. In natural photosynthesis solar energy is used to produce biomass, hydrogen and oxygen.

The entire photosynthesis process can be broadly divided into three distinct steps [21]:

i. *light harvesting process*, where *'antenna' absorbs photons, induces formation of high energy electron-hole pair and local charge separation in Photosystem I (P.S-I)and Photosystem II (P.S-II),*
ii. *larger extent of spatial charge separation through proton coupled electron transfer (PCET) between redox cofactors along the photosynthetic chain,*
iii. *generation of H_2 and O_2 at remarkable enzymatic sites (such as Fe- Fe cluster in Hydrogenase for hydrogen and $CaMnO_4$ centre for oxygen evolution) through multi-electronic redox catalysis,*

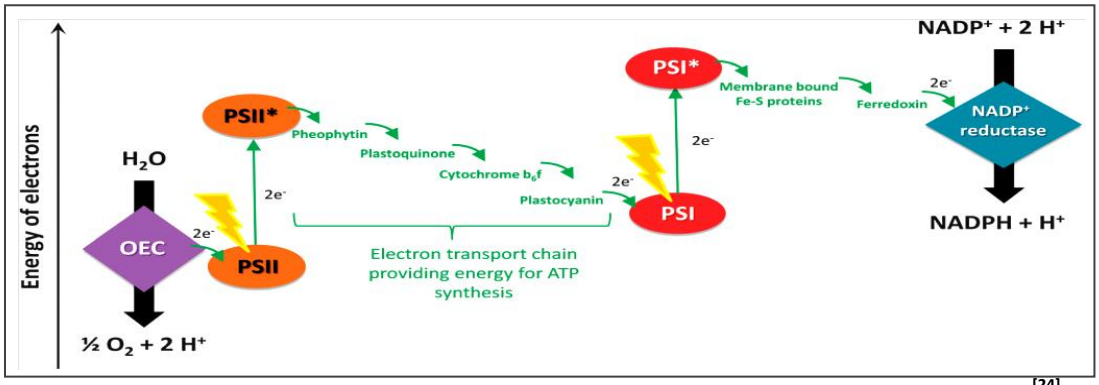


Fig. 1.3 Schematic Representation of Electron Transfer during Photosynthesis (Z- scheme) [24]

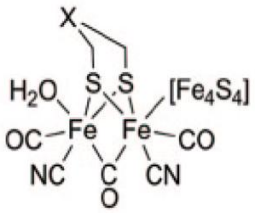
1.5 NEW HORIZON: *Bioinspired Materials*

Natural photosynthesis is emerging as a fascinating source of inspiration for designing of systems that are able to achieve efficient light-to-hydrogen production based on the advantages of PEC technology [23;24]. Bioinspired materials are the novel materials which mimic the functional trick (minimal structure required for a catalyst to achieve the biological function) of an active site which are responsible for carrying out oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).

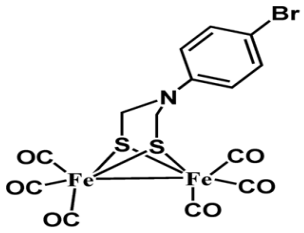
The bioinspired approach does not aim at imitating/replicating the exact details of an active site, instead it attempts to exploit its basic chemical principles, on which a much larger chemical space can be explored, to enrich chemistry with new catalysts and exciting reactions. Bioinspired approach implies that the increased understanding, at the molecular level, of a given biological catalyst is exploited not only to reproduce it synthetically in a much simpler form (biomimetic chemistry), but also to explore innovative combination of atoms and molecules in the formation of the mimic [24].

For example, in nature, Hydrogen is utilized/produced efficiently by Hydrogenase enzymes which are metalloenzymes employing Fe/Ni. They efficiently and reversibly catalyze the conversion of H_2 into 2 electrons and 2 protons.

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$



Active site of Hydrogenase



Mimic of Hydrogenase [25]

Four important components are required to develop Bioinspired Photoelectrochemical system for efficient Hydrogen production [26]:

i. *a promising light harvesting material with high molar extinction co-efficient (ε);*
ii. *effective charge separation through a molecular donor–acceptor pair;*
iii. *a crude and highly efficient water oxidation catalyst; and*
iv. *a semiconducting material as a light absorber as well as substrate*.

The development of a novel energetic scenario based on the use of two renewable resources, water and sunlight, is a challenging solution to the energy crisis the world is currently facing. Biologically inspired methods and materials are presented as new tools for the design of novel photoelectrochemically active materials, focusing on the advantages for PEC technology. The need for cost-effective, high-performance material is driving the contemporary PEC research, with the expectation that advances in the methods will bring the necessary change that is required for the commercialization of this technology.

Present work is an attempt to study the role of bioinspired materials in conjunction with semiconductors in photoelectrochemical splitting of water.

2. LITERATURE REVIEW

Application of bioinspired materials in the field of hydrogen generation is a new and developing area of interest. Scientists from all over the world are trying to exploit its efficiency of bioinspired materials in the area of PEC water splitting for hydrogen production. Some of the recent work has been summarised below:

Ihara *et al.* (2006) [27] reported the first example of a direct light-to-hydrogen conversion system using hydrogenase and Photosystem I. They designed an artificial fusion protein composed of the membrane-bound [NiFe] hydrogenase from and the peripheral PS I subunit. After spontaneous association with PS I, the resulting hydrogenase—PS I complex displayed light-driven hydrogen production at a rate of 0.58 µmol of H_2 (mg of Ch1)$^{-1}h^{-1}$ in presence of ascorbic acid, DTT and TMPD (electron donor system).

Badura *et al.* (2006) [28] succeeded in attaching a Photo system II modified with an *His* tag (isolated from the cyanobacterium) onto gold electrodes modified with thiolates bearing terminal Ni(II)- nitrilotriacetic (NTA) acid groups. The surface coverage was found to correspond to one monolayer and upon illumination in the presence of 2,6-dichloro-1,4-benzoquinone as the electron mediator, generation of a photocurrent up to 14 µA cm^{-2} was observed. When higher amount of enzyme was grafted, high photoactive current of 45 µA cm^{-2} was obtained.

Dismukes *et al.* (2009) [29] reported a synthetic $Mn_4O_4L_6$ cubane-like complex, bearing diarylphosphinate ligands which convert its bridging oxides into O_2 upon photo-oxidation in the gas phase. Binding of the oxidized form of this complex, i.e. $[Mn_4O_4L_6]^+$, to a thin proton-conducting Nafion membrane deposited on a conducting glassy carbon electrode yields a robust catalyst that sustains the photoelectro-oxidation of water to O_2. When this electrode is polarized above the $[Mn_4]^{2+}/[Mn_4]^+$ potential at 1.00 V vs Ag/AgCl (electrical bias) and illuminated with filtered Xe light (λ > 275 nm), a large photocurrent is observed corresponding to the formation of O_2. This oxygen was found to be derived from water using labelling experiments. Catalytic turnover frequencies were found to be of 20–270 per Mn_4 unit and per hour and turnover numbers > 1000.

Heberle *et al.* (2009) [30] used the membrane-bound hydrogenase (MBH) from Eutropha H16 and fused it with an extrinsic subunit of a histidine-tagged form of PS I. This system was then immobilized at the surface of a nickel-functionalized gold electrode through a nickel His-Tag interaction. When this electrode was poised at -0.09 V vs NHE, to reduce the soluble electron carrier N-methylphenazonium methyl sulfate (PMS), and under visible illumination (λ_{max} = 700 nm), photocurrent of 85 nA cm^{-2} was observed, 30% of which being assigned to the hydrogen evolution reaction.

Golbeck *et al.* (2010) [31] has developed a strategy to connect an Hydrogenase to a purified natural photosynthetic component. A dithiol molecule is employed to link via Fe-S coordination

bonds a [4Fe-4S] cluster of a mutant of the PS I subunit to the distal [4Fe-4S] cluster of a mutant of the [FeFe]-hydrogenase (from C. acetobutylicum). Direct electron transfer was established between the two components, resulting in the production of hydrogen under illumination at a rate of 30.3 µmol of H_2 (mg of Ch1)$^{-1}$ h^{-1}, at pH = 8.3 in the presence of a combination of cytochrome c_6, ascorbate and phenazine methosulfate as sacrificial electron donor system. This PhotoS I - Hydrogenase system has been found to display a remarkable stability and remained active for more than 2 months, in the absence of oxygen.

Spiccia *et al.* (2010) [32] reported photoanode based on a bioinspired cubane cluster, entrapped in a nafion matrix, and deposited onto a TiO_2-supported ruthenium photosensitizer. This photoanode has successfully coupled to a platinum counter-electrode and photocurrents up to 25 µA cm^{-2} were generated under illumination together with evolution of oxygen.

Sun *et al.* (2010) [33] put forth a photoelectrochemical device based on the same design as reported by Spiccia [31]. A molecular mononuclear Ru catalyst bearing carboxylate ligands was embedded in Nafion membrane and deposited on a dye-sensitized nanostructured TiO_2 film. This assembly provided the photoanode whereas a Pt foil was used as cathode. Splitting of water from a neutral aqueous electrolyte was observed on supplying small voltage bias.

Wang *et al.* (2011) [34] proposed a system that represents a significant breakthrough for photocatalytic H_2 production by a hydrogenase mimic. Nanocrystal quantum dots of CdTe were used to capture visible light. Excited electrons were transferred to the [FeFe]-hydrogenase active site mimic and ascorbate as electrolyte provided electrons to fill holes. Three hydrophilic ether chains were attached via a cyanide group in order to enhance the aqueous solubility of the catalyst. The system produced H_2 steadily for 10 h with a turnover frequency of 50 h^{-1}.

Nocera *et al.* (2011) [35] reported Cobalt hangman corrole, bearing β-octafluoro and *meso*-pentafluorophenyl substituents, as an active water splitting catalyst. When immobilized in Nafion films, the turnover frequencies for the $4e^-/4H^+$ process at the single cobalt center of the hangman platform approaches 1 s^{-1}. The water splitting reaction was found to be pH dependent which suggests that a proton-coupled electron transfer (PCET) catalytic mechanism is operating.

Chorkendorff *et al.* (2011) [36] came up with bioinspired molecular clusters based on molybdenum and sulphur, evolving hydrogen at rates comparable to that of platinum. The incomplete cubane-like clusters (Mo_3S_4) efficiently catalyze the evolution of hydrogen when coupled to a *p*-type Si semiconductor that harvests red photons in the solar spectrum. The current densities at the reversible potential match the requirement of a photoelectrochemical hydrogen production system with a solar-to-hydrogen efficiency in excess of 10% and exhibiting photocurrent density of the order of~ 8mA cm^{-2}.

Nocera *et al.* (2011) [37] have also designed a solar water splitting device that avoids the use of expensive noble metal catalysts, instead they used the earth-abundant Cobalt–Phosphate (Co-Pi) catalyst for water oxidation, and a NiMoZn-alloy as a Hydrogen production catalyst. In their

'artificial leaf', visible light is absorbed by amorphous triple-junction silicon deposited onto a stainless steel support and coated with an indium tin oxide (ITO) layer. The device achieved solar-to-hydrogen efficiencies of 4.7% and 2.5% for the wired and wireless configurations respectively. The 3jn-a-Si produces 8mA cm^{-2} of current at 1.8V bias voltage.

Braun *et al.* (2012) [38] reported that Phycocyanins have light harvesting properties and belong to the class of Phycobilisomes protein. When they were covalently cross coupled with hematite, increase in photocurrent was observed. The hematite- phycocyanin integrated system was formed by the consecutive adsorption and cross coupling of protein molecules, separated by agarose layer and a linker molecule. This assembly showed two - fold increment (0.87mA cm^{-2}) in the photocurrent with respect to the pristine hematite film (0.49mA cm^{-2}). Also, the assembly showed long term stability and a promising bioinspired photoanode for PEC application.

Zhang *et al.* (2014) [39] have recently reported work on Cobalt−oxo cubane clusters immobilized on a Nafion film coated fluorine-doped tin oxide (FTO) electrode and an α-Fe_2O_3 photoanode as surface catalyst for water oxidation. Efficient visible light-driven water oxidation was realized by coupling molecular cobalt oxo cubane electrocatalyst with an α-Fe_2O_3 semiconductor as a noble metal-free photoanode, showing that stability significantly improved with respect to that of the homogeneous system. α-Fe_2O_3 at a bias of 0.5 V versus Ag/AgCl showed six fold increase in the photocurrent.

3. PRESENT WORK

With the motivation drawn from the above mentioned reports using bioinspired materials in the PEC water splitting, the present work is proposed to be carried out using bioinspired material in conjunction with the semiconductors systems towards improving the efficiency of solar driven water splitting for hydrogen production.

It is proposed to study Phycocyanin, Hydrogenase and other such bioinspired materials along with semiconductors such as TiO_2, ZnO, CuO, Si etc. which are easily available, economical and are currently being investigated in the PEC water splitting research.

4. OBJECTIVES

4.1 Preparation of nanostructured thin film semiconductor electrode such as *CuO, ZnO, TiO_2* etc. using spray pyrolysis or sol – gel method on substrates like p-silicon, FTO or ITO.

4.2 Fabrication of bioinspired catalysts e.g. *Phycocyanin*, *Hydrogenase* etc. on the prepared semiconductor thin film.

4.3 To study the stability of so prepared semiconductor-bioinspired catalyst system.

4.4 Characterization of the so formed semiconductor will be done with the help of :

(a) X- Ray Diffractometer (XRD) to determine the crystallinity and grain size.

(b) Scanning Electron Microscopy (SEM) to obtain the morphology.

(c) Atomic Force Microscopy (AFM) to obtain 3-D surface topography and roughness.

(d) UV – Visible Spectroscopy to obtain the band gap of the material.

4.5 Photoelectrochemical (PEC) study of the samples in alkaline and in acidic buffer medium.

4.6 Hydrogen detection with the help of Gas Chromatograph (GC).

4.7 Calculation of Induced Photon to Current conversion Efficiency (IPCE).

5. PROPOSED METHODOLOGY

5.1 Preparation of Samples:

Nanostructured thin films would be prepared using sol-gel or spray pyrolysis. Semiconductor thin films would be deposited either on indium tin oxide (ITO) or on fluorine doped tin oxide (FTO).

Pellet semiconductor electrode would also be prepared using sol gel route. Surface of the samples will be modified by fabricating bioinspired catalysts using Phycocyanin, hydrogenase mimic etc.

5.2 Characterization:

a. Average particle size and crystal phase will be analysed through ***Bruker AXS-D8 Advance*** X-ray Diffractometer. Scherrer equation ($0.9\lambda/\beta\cos\theta$) will be employed to calculate the average particle size.
b. Morphology and topography of the so prepared samples would be studied through ***Scanning Electron Microscope (SEM)*** and ***Atomic Force Microscope (AFM)***.
c. UV- visible absorption study for bandgap measurements would be done through ***UV-Vis spectrophotometer***.

5.3 Photoelectrochemical Studies

PEC studies will be carried using bioinspired fabricated electrodes which will work as working electrode. Standard calomel electrode will act as reference electrode while Platinum electrode will be used as counter electrode. The pH of electrolyte will be varied from acidic to basic medium.

I-V characteristics will be obtained under both dark and irradiated conditions using ***Zahner Electrochemical Workstation*** and 300 W Xenon or Tungsten light source.

5.4 Efficiency Calculation :

The efficiency of the system would be measured in terms of:

a. solar-to-hydrogen conversion efficiency (STH)

$$\mathbf{STH} = \left[\frac{(\mathbf{mmol\ H_2\ /s}) \times (\mathbf{237\ kJ/mol})}{\mathbf{P_{Total}\ (mW/cm^2)} \times \mathbf{Area(cm^2)}}\right]_{\mathbf{AM\ 1.5G}}$$

b. incident photon-to-current efficiency (IPCE)

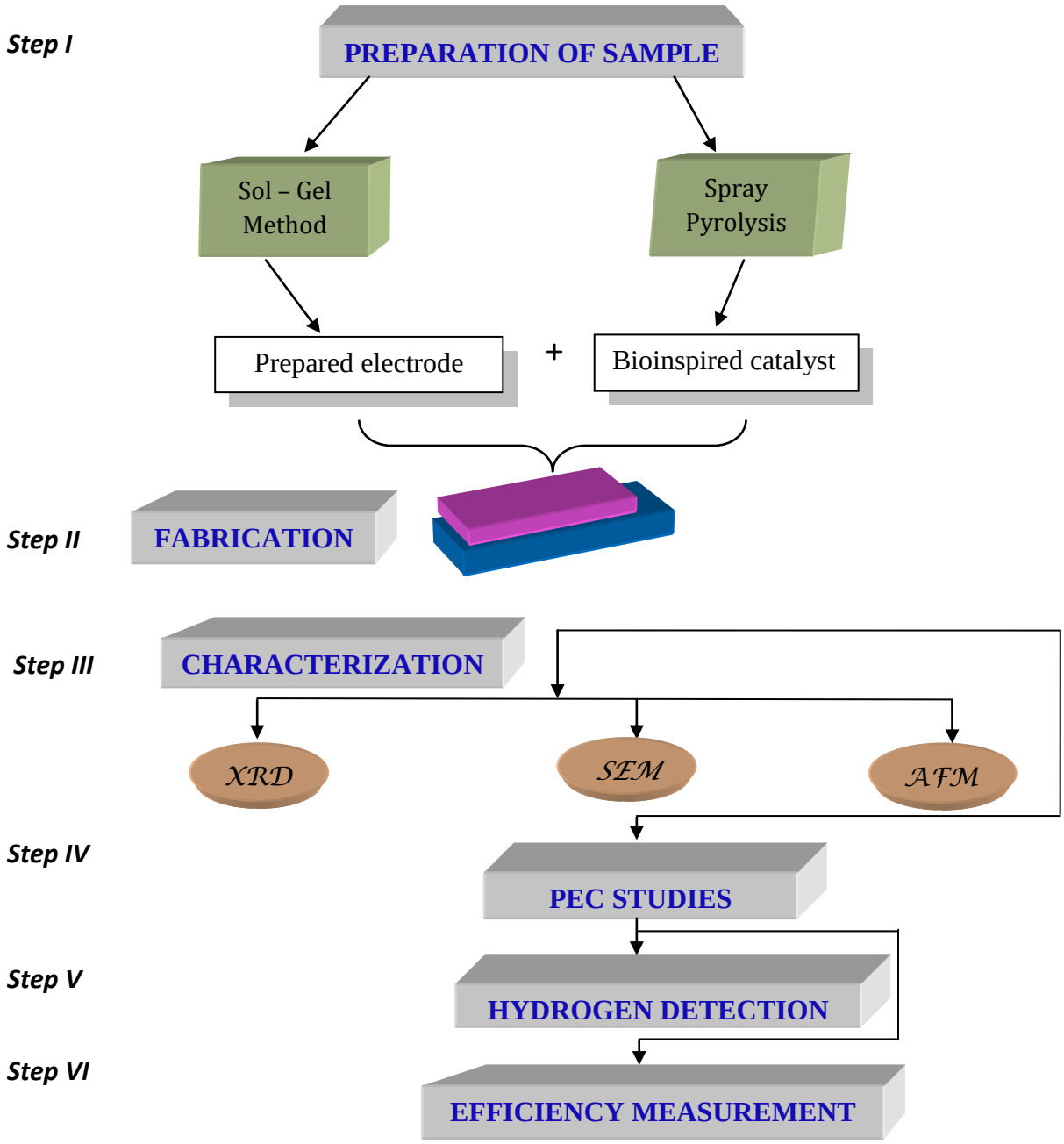
IPCE describes the maximum possible efficiency with which incoming radiations can produce hydrogen from water.

$$\mathbf{IPCE(\%)} = \frac{\mathbf{1240} \times \mathbf{I_{SC}\,(A/cm^2)}}{\boldsymbol{\lambda}\mathbf{(nm)} \times \mathbf{I_{inc}(W/cm^2)}} \times \mathbf{100}$$

5.5 Hydrogen Detection :

Efforts would also be made to collect the evolved gases from PEC cell and pass them through alkaline pyrogallol solution at 0-5°C to remove oxygen. Rest of the gas (largely hydrogen) would then be collected in a gas measuring tube, slowly, by displacing the water. The collected gas would be qualitatively analyzed for hydrogen by employing ***Perkin Elmer - Claurus 580 Gas Chromatograph***.

6. PLAN OF ACTION



7. PILOT STUDY

Working electrodes for use in PEC studies were prepared using p-silicon wafer substrate and hydrogenase mimic catalyst (obtained from Indian Association for the Cultivation of Science, Kolkata). The catalyst was fabricated over the substrate by drop casting method. Prior to this, catalyst was dissolved in Methanol + Dichloromethane + Nafion solution in a ratio of 7:2:1 such that solution contained 0.5% nafion [35].

The band gap of the photocatalyst as determined using UV-Vis spectroscopy, offered λ_{max} in the UV region (350nm). Further, characterization was done using X-ray Diffractometer and scanning electron microscope and the results are being analysed.

Photoelectrochemical studies were performed using three electrodes system viz.; platinum as counter electrode, Calomel as reference electrode while working electrode was the catalyst fabricated over p type silicon wafer. The experiment was carried out under both dark and illumination using 0.1N H_2SO_4 (pH 2) as electrolyte. Significant photocurrent was obtained upon illuminating the working electrode and results were reproducible upto 7 days.

Similar studies using different substrates and other bioinspired mimics are underway.

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